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(54) ORE PELLET AND METHOD FOR PRODUCING SAME

(71) We, KUREHA KAGAKU KOGYO KABUSHIKI KAISHA, a joint-stock company of Japan, located at 8, 1-Chome, Nihonbashi Horidome-Cho, Chuo-Ku, Tokyo-To, Japan, and KAWASAKI STEEL CORPORATION, a joint-stock company of Japan, of 1,1-Chome, Kita-Ho Machidori, Fukiai-ku, Kobe-Shi, Hyogo-Ken, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The present invention relates to pellets or briquettes obtained by binding fine ore with addition of a sulfonic acid of a condensed polycyclic hydrocarbon or its salt as a binder, and then subjecting the pelletized ore to drying and firing processes.

Hitherto, pig iron has been produced by charging iron ore into a smelting furnace together with coke to reduce the iron ore.

Recently, it has become more and more difficult to obtain high grade iron ore rich in iron content, and even when such iron ores can be obtained, they usually have to be transported from a considerable distance in the form of fine ore. In other words, there has been an increased tendency to use only the fine ore with high iron content. Such high grade fine ore is obtained by subjecting crude iron ore to crushing and grinding at the mining site or from fine iron ore produced at the time of mining in such processes as, for example, magnetic separation.

As is clear from the above, it is of real advantage to obtain fine iron ore containing as high a grade of iron as possible rather than to rely on poor ore (or low grade ore) especially when transported at a considerable expense. However, when this fine ore is directly charged into a smelting furnace as it is, it prevents the blast air from smoothly and uniformly flowing within the furnace and also prevents ore particles from contacting a reducing

gas, whereby satisfactory continuous operation of the blast furnace is made difficult.

In order to solve the above-mentioned problem, it has been the practice to attain efficient production of pig iron by pelletizing such fine ore into pellets or briquettes of a certain definite size, and charging these into a blast furnace. In this case, the size of the pellets or briquettes is determined by a balance between the velocity of the reducing gas passing through the blast furnace and reduction speed of the iron ore pellets or briquettes. In general, spherical pellets of 15—20mm in diameter are used.

The above-mentioned pelletized ores should have a sufficient mechanical strength so that they are not broken when they are charged into the blast furnace. They must also have a sufficient compressive strength to withstand the external mechanical stress applied in the course of drying and firing processes at the time of pelletization as well as to withstand the thermal shock caused by rapid heating to a high temperature.

For the purpose of pelletizing fine iron ore, bentonite has heretofore been used as an additive, in an amount of about 1% in the case of the fine iron ore containing some amount of moisture. While bentonite often exhibits an excellent binding property, this is considerably variable depending upon the place of origin thereof, on account of which the acquirement of bentonite of uniform quality is very difficult.

Moreover, although bentonite itself is a natural resource and hence of low cost, the recent trend is that, due to shortness of labour, the expense of mining the natural product gradually increases and hence the market price of the product is becoming higher. In other words, the present situation is such that, as the quantity of bentonite necessary for iron-making is very large, it has become extremely difficult to ensure constant acquirement at a low price of bentonite having a uniform quality for use as a binder for pelletization.

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On the other hand, the purity of the pelletized ores is lowered by the addition of bentonite, since this constitutes an impurity, whereby the coke ratio in the blast furnace is increased thereby hindering productivity. Furthermore, the addition of the bentonite necessitates the further addition of lime to increase the fluidity of the slag and separation of the metal from the slag.

Under such circumstances, an inexpensive binding agent having a constant and uniform quality is particularly demanded in this field of industry. It is also required that such a binding agent should perfectly decompose in the course of pelletization (i.e. in the firing process) and not leave any residue whatsoever.

Therefore, it is an object of the present invention to provide pellets or briquettes of ores of various sorts, which are produced by the use of a particular binding agent to be described hereinafter.

It is another object of the present invention to provide ore pellets or briquettes having a minimum swelling property when treated in a blast furnace as well as having high compressive strength.

It is still another object of the present invention to provide a method for producing such ore pellets by utilizing such a binding agent.

Characteristic features, functions and advantages of the invention will become apparent from the following detailed description of the invention.

A new and inexpensive binding agent suitable for producing ore pellets or briquettes has been discovered by the present inventors as a result of their various experiments and studies. As this binder is a synthetic product, its quality and low price can be always maintained. Also it is excellent in its pelletizing effect, and perfectly decomposes in the firing process without leaving residues in the resulting product. Furthermore, as the binder can be used in the liquid state, it provides great advantages in that it can be easily transported through pipe lines, which not only facilitates material handling, but also enables uniform mixing of the binder with the fine ore to be automatically controlled, as well as improving the working circumstances.

The binder to be used in the present invention consists of sulfonic acids derived from a mixture of condenser polycyclic hydrocarbon compounds or the salts of such acids. The condensed polycyclic compound is obtained by subjecting a hydrocarbon oil to a heat-treatment at a high temperature. The hydrocarbon oil used herein as the raw material is to be understood as including crude oil or its distillates, extracts and residual materials which are obtained by distillation or extraction of crude oil, such as, for example, gas oil, kerosene, naphtha, heavy oil, asphalt and asphaltene. Moreover, decomposed oil which is a by-product of naphtha cracking for production of

olefin, or its distillate or residual materials can be used. Furthermore, coal tar obtained from coal can be used as the raw material.

The method of preparing the binder according to the present invention will be described hereinbelow.

The raw material is used singly or in the form of a raw mixture with other raw materials. This raw material or raw mixture is firstly subjected to heat-treatment for a reaction time of from 0.5 to 0.0001 second, preferably from 0.1 to 0.005 second at a temperature of from 700° C. to 2,000° C. by means of an external heating method using a pipe-heater, or an internal heating method using a high temperature gas such as superheated steam or flame, and then the heat-treated raw material is cooled by an appropriate method to separate gaseous substances such as olefins, thereby producing a tarry residue. This residue itself or its distillates and/or distillation residue (which is a pitch) are made the raw material for the subsequent sulfonation.

The material for sulfonation which is obtained in the above heat-treatment conditions has been verified by various sorts of measurements such as infrared absorption spectrum, N.M.R. (nucleomagnetic resonance absorption spectrum), gas chromatograph, elementary analysis, molecular weight, and molecular weight distribution, etc. to be a substance of high aromaticity having characteristics which are always closely similar irrespective of which of the various kinds of raw materials mentioned above have been used.

The above-mentioned material has the following structure and composition, viz., it is a mixture of substances each having a condensed polycyclic structure containing more than two rings and a number of aliphatic chains as its principal constituent, the mean molecular weight and H/C atomic ratio of the material being 160—5,000 and 0.3—1.25, respectively. The upper limit of the mean molecular weight and the lower limit of the H/C atomic ratio are determined as the limits capable of producing a water-soluble sulfonated substance, while the lower limit of the mean molecular weight and the upper limit of the H/C atomic ratio are determined by a critical point, at which the thus obtained sulfonated substance loses its effectiveness as a binding agent. The binder material is not a single substance, but rather is a mixture of substances.

This high aromatic material is then subjected to a sulfonation treatment. This treatment can be easily carried out by sulfuric acid, fuming sulfuric acid, sulfuric anhydride, chlorosulfonic acid, or any other sulfonating agents which are generally used.

Sulfonation conditions depend upon the kind of the sulfonating agent to be used. In general, the stronger the sulfonating agent to be used is, the milder should preferably be

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- the reaction conditions: If necessary, the reaction may be carried out in an appropriate solvent. For example, it can be carried out in a single or mixed solvent which does not, or is difficult to, react with the sulfonating agent. Examples of such solvents are: (1) paraffins or cycloparaffins such as n-hexane or cyclohexane; (2) halogenated aliphatic hydrocarbons like chloroform, carbon tetrachloride, ethylene dichloride, ethane dichloride, and ethylene tetrachloride (perchloroethylene); (3) aromatic halogenated hydrocarbons like ortho-dichlorobenzene; (4) or dioxane, pyridine, nitrobenzene, or liquid sulfuric acid.
- The reaction temperature also depends upon the kind of reagent and the intended degree of sulfonation, although a very wide range of from -20° C. to 200° C. can be generally adopted. Though the degree of sulfonation may be arbitrarily controlled by suitably selecting the kind of sulfonating agent and the reaction conditions, it is preferred that the sulfonation should be necessarily continued until substantial parts (more than 70%) of the high aromatic hydrocarbon material is converted to be water-soluble. This degree of sulfonation, on the other hand, can be represented in terms of the sulfur content in the sulfonated product, which will be from 10—30 weight percent.
- After the sulfonation treatment is complete, the sulfonated substance can be used as it is, but when the substance is further neutralized with any organic or inorganic basic material such as caustic soda, caustic potash, calcium hydroxide, ammonia, sodium phosphate, triethanolamine, or morpholine, the corresponding sulfonates can be obtained and these may also be used in the method of the invention.
- On the other hand, depending on the circumstances, not only a single kind of salt, but also a mixture of more than one kind of basic substance can be added to the sulfonated substance to neutralize it so as to augment the effect of the sulfonate as the binding agent.
- On neutralization there is produced from time to time a salt as a by-product owing to the presence of excess of the sulphonating acid. This by-product salt may be used as it is, or may be separated from the sulfonate depending on necessity.
- The sulfonic acid or sulfonate of the polycyclic aromatic substance thus obtained is added to fine ores in an amount in the range of from 0.05 wt. % to 4.0 wt. % with respect to the fine ore. A preferable range is from 0.1 to 2.0 wt. %. With an added quantity below 0.05%, the binding action cannot be sufficiently exhibited, while, with the quantity above 4.0%, the binding action is sufficiently exhibited, but the economic merit of providing the low-priced binder would be reduced. The particle size of the fine iron ore is preferably below 325-mesh (Tyler standard).
- The sulfonic acid or sulfonate of the poly-
- cyclic aromatic substance can be added either alone to the fine iron ore, or in conjunction with other binders such as bentonite, clay, sulfonated lignin, cement binder, or with a surface active agent. Furthermore, the sulfonic acid or the sulfonate may be used together with an additive such as lime (usually in the form of CaCO_3), or calcium hydroxide, in a quantity of 2—10 wt. % with respect to the quantity of the fine iron ore.
- As mentioned above, the sulfonic acid or its salt obtained by heat-treatment and subsequent sulphonation of petroleum hydrocarbon or coal hydrocarbon has been found to have various advantages such as that it can be inexpensively and easily produced, it exhibits a remarkable binding effect when used to pelletize fine iron ore, by which excellent pellets or briquettes can be produced from the fine ore. Such excellent binding action is applicable not only in pelletizing fine iron ore, but also in pelletizing other mineral ores such as ores of zinc or copper. It has been confirmed that excellent pellets similar to that in the case of iron ore can be obtained with these ores.
- It is surprising to note that the iron ore pellets according to the present invention also have the very advantageous property such that, when the pellets are subjected to reduction, the minimum degree of swelling occurs. Accordingly, there is no possibility of the furnace operation being hindered due to the swelling or breakage and disintegration due to decreased mechanical strength through swelling, of the pellets, in the course of the reduction, and hence there is effective utilization of the pellets in the furnace.
- It is furthermore possible to convert these pellets into reduced pellets having large apparent specific gravity and high mechanical strength by subjecting the pellets to reduction in an atmosphere containing a reducing gas such as hydrogen or carbon monoxide by utilizing various reduction furnaces. The reduced pellets thus obtained can be directly utilized as a raw material for steel-making.
- In the present invention, even when powdery carbon material such as coal or coke are mixed with the fine iron ore in a quantity of less than 20 wt % with respect to the quantity of the fine ore, pellets having excellent mechanical strength, reducibility, and a minimal swelling property can be obtained.
- As is clearly understood from the above-mentioned facts, the ore pellets and reduced pellets according to the present invention would greatly contribute to the iron and steel industries of the present and future, where the utilization of fine ores has been taken up as an important problem in the world.
- Table 1 indicates in sequence the kind of raw material used for the sulfonation, the method of heat-treatment and its conditions, the distillation conditions of the heat-treated

material, the method of sulfonation, and the kinds of resulting salt.

Tables 2 to 4 indicate test results of the binding effect of the binding agent with respect to fine iron ore in comparison with that of bentonite.

The heat-treatment of the raw materials shown in Table 1 was carried out according to two methods; the one is to treat the raw material with super-heated steam obtained by a pebble-type regenerative furnace, and the other is to treat the raw material by jetting the same out into a flame, in which no excess oxygen exists. The first-mentioned method is indicated in Table 1 as "Steam", and the second-mentioned method as "Flame". The tarry substance obtained at this time is also classified according to the three cases of: (1) directly subjecting it to the sulfonation without distillation; (2) subjecting it to distillation under a normal or a reduced pressure, and then subjecting a distilled component to the sulfonation treatment; and (3) subjecting it to distillation under a normal or a reduced pressure, and then subjecting the distillation residue from the distillation to the sulfonation treatment.

The sulfonation treatment was conducted by first dissolving or suspending the tarry substance, or its distilled components, or its residue after distillation in ethane dichloride in an amount approximately four times as much as the raw material, and then blowing into this solution or suspension gaseous sulfuric anhydride in the case where the sulfonation reagent is sulfuric anhydride, or blowing thereinto fuming sulfuric acid, or chlorosulfonic acid, or sulfuric acid in the liquid state in the case where the sulfonation reagent is any one of these acids.

When the thus-obtained sulfonated material is to be used in the form of a salt, ammonia water, caustic soda aqueous solution, or calcium hydroxide is added to neutralize the acid so as to obtain the corresponding sulfonates.

With this sulfonated compound as the binding agent, dry balls for measuring the rupture strength of ore pellets were produced in the following manner. Fine powder (specific surface area 2,300 cm²) of magnetically dressed iron ore concentrate of Canadian origin was preliminarily dried so as to contain therein a certain definite quantity of moisture, after which the binding agent of predetermined quantity in the form of powder or aqueous solution was added to the concentrate, while adjusting the total moisture content to a definite level (approx. 8.5%) in either case.

The same procedure was followed in the cases of using bentonite, or other additives alone, or using the binding agent of the present invention and bentonite or other additives in combination.

Next, pelletization was carried out by operating a disk-type pelletizer of 260 mm in inner diameter and 60 mm in depth, inclined at 45 degrees, and rotating at a rate of 18 rpm. After 15 minutes' operation, pellets of 16 mm in diameter were obtained.

Then, the pellets were dried for 12 hours at 105° C. in a hot-blast type isothermal drier. After the drying, the rupture strength of the dry balls was measured by using a strength measuring instrument according to an ordinary method. Further, the dry balls were placed in a container made of stainless steel wire net and fired at 1,200° C. to make the fired pellets.

The test results on these dry balls and fired pellets are as consolidated in Tables 1 through 4. It is clearly recognized from the Tables that the strength of green balls and dry balls is improved by applying the method of the present invention. Moreover, these green balls and dry balls are found to be sufficiently durable against external mechanical force, while they are being treated in the drying and firing furnace, so that they are practically useful even in the blast furnace operation.

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TABLE 1

Example No.	Raw Material	H/C ratio	Mean molecular weight	Heat Treatment Method	Temperature (°C)
1 1	Crude oil of Khafji origin	0.55	1200	Steam	approx. 1,550
2	Naphtha	0.81	600	Flame	1,200
3	Burner fuel oil	0.90	520	Steam	1,000
4	Straight asphalt	0.74	980	Flame	950
5	S & W * Bottom oil	0.88	580	Flame	900
6	Coal tar oil	0.75	250	Steam	759

* Stone-Webster type cracking furnace bottom oil.

Time (m. sec. i.e. $1/1000$ sec.)	Distillation Conditions (indicated in terms of nor- mal pressure conversion)	Sulfonation Treatment			Kind of Salt
		Reagent	Temp. (°C)	Time (Hr)	
5	450° Distillation residue	SO ₃	60	2	Na
5	Not distilled	Sulfuric acid (98% conc.)	80	6	Na + Ca** (50 : 50)
5	250°C Distillation residue	Fuming sulfuric acid (specific gravity 1.86)	5	4	NH ₃
5	350°C Distillation residue	Chlorosulfonic acid (100%)	20	6	Na
2	450°C Distillation residue	SO ₃	55	1.5	Ca
2	350° — 450°C Distilled components	Fuming sulfuric acid (specific gravity 1.86)	0	6	—

** mol ratio.

TABLE 2
Dropping Strength of Green Balls (S, units: number of times)

Example No.	Adding Quantity of Binding Agent (wt %)							Binder of the present invention (0.05%) plus bentonite (0.5%)
	0	0.05	0.1	0.3	0.5	1.0	2.0	
1	3.5	2.7	3.8	4.0	4.1	4.3	4.7	3.7
2	3.2	3.5	3.7	4.2	4.5	4.8	4.9	3.6
3	3.0	3.3	3.7	4.0	4.3	4.4	5.0	3.4
4	3.4	3.5	3.6	4.3	4.5	4.6	4.7	3.4
5	3.5	3.7	3.8	4.1	4.3	4.7	4.5	3.6
6 *	3.3	3.6	3.8	4.0	4.1	4.3	4.5	3.6
7 **	3.2	3.3	3.6	4.0	4.2	4.3	4.4	—
8 **	3.0	3.2	3.5	3.8	4.0	4.2	4.3	—
Reference ex. (only bentonite)	3.3	3.4	3.6	—	3.7	4.3	—	—

Examples 1 to 5 use the binders of Examples 1 to 5 respectively of Table 1.

(Note) * The fine powder of copper pyrite was used instead of magnetically dressed iron ore concentrate.

** 2.9 weight % of pulverized lime was added to the magnetically dressed iron ore concentrate.

*** 10 weight % of pulverized coke was added to the magnetically dressed iron ore concentrate. (The same binder as in Example 1 of Table I was also used in Examples 6, 7 and 8).

The dropping strength was measured in the following manner: twenty balls were dropped onto an iron plate of 4.5 mm thick from a height of 45 cm; if the number of balls broken at the n th time is represented by N_n and the strength by S , the strength can be obtained from the following equation:

$$S = \frac{\sum n_i N_i}{20}$$

(Rounded to decimal two places, and indicated with the number of times.)

TABLE 3
Compressive Strength of Dry Balls (kg/pellet)

Example No.	Adding Quantity of Binder (wt %)							Binder of the present invention (0.05%) plus bentonite (0.5%)
	0	0.05	0.1	0.3	0.5	1.0	2.0	
1	1.3	3.1	4.7	9.3	11.5	31.1	59.4	3.3
2	1.4	2.9	4.5	8.9	11.2	30.5	58.6	3.0
3	1.3	2.7	4.1	8.0	11.0	29.5	57.9	2.9
4	1.5	2.5	3.9	8.0	10.5	29.7	57.9	2.8
5	1.3	2.8	4.0	8.5	10.5	28.9	58.4	3.1
6	1.4	2.9	3.9	8.1	10.7	29.4	59.1	3.1
7	1.5	3.2	4.9	9.7	12.1	32.4	62.4	3.3
8	1.3	2.7	3.9	7.8	10.2	28.6	54.1	2.8
Reference Ex. (bentonite)	1.3	1.5	1.6	—	2.5	4.0	—	—

Note: Examples 1 to 5 use the binders of Examples 1 to 5 respectively of Table 1.
Examples 6, 7 and 8 use the binder of Example 1 in Table 1.

TABLE 4
Compressive Strength of Fired Pellets (kg/pellet)

Example No.	Adding Quantity of Binder (wt %)							Binder of the present invention (0.05%) plus bentonite (0.5%)
	0	0.05	0.1	0.3	0.5	1.0	2.0	
1	x	300	320	290	300	310	330	300
2	x	—	300	—	—	—	—	—
3	x	—	310	—	320	—	—	300
4	x	—	290	—	—	—	—	290
5	x	290	300	310	310	310	320	280
6	—	—	—	—	—	—	—	—
7	x	—	300	—	—	320	—	—
8	x	—	—	—	—	—	—	—
Reference Ex. (bentonite)	x	x	x	300	290	310	—	—

Note: Examples 1 to 5 use the binders of Examples 1 to 5 respectively of Table 1.
Examples 6, 7 and 8 use the binder of Example 1 of Table 1.

(Note)

1. "x" signifies that the pellets were broken or cracked during the firing operation and could not retain their shape until the measurement of strength.
2. Further for the materials of Examples 1 and the Reference Examples shown in Table 4, a reduction test was carried out in accordance with Japanese Industrial Standards JIS M8713 with the fired pellets where the quantity of the binder added was 0.5 wt %. That is, 500 gr. of the dry balls were placed in a reaction tube (75 mm in inner diameter) made of heat-resistant steel plate (JIS G4304), then while causing a mixture gas of 30 vol % of carbon monoxide and 70 vol % of nitrogen to flow through the reaction tube at a rate of 15 l/min. the heating temperature was raised rectilinearly up to 900° C in two hours, at which the reaction material was kept for 30 minutes. From the weight measurements made before and after this heat-treatment, the rate of reduction was calculated. Further, the swelling index was measured in accordance with JIS M8715, and the rupture strength was also measured. These results are shown in Table 5. In the case of the present invention, the swelling index is found to be small, the rupture strength to be large, and the rate of reduction to be high. This means that the reduced pellets of superior quality can be obtained by the present invention.
3. The test for the compressive strength of dry balls and fired pellets was conducted by placing a ball or pellet between two flat metal plates, and then applying compression force on both plates against the test material to find out the point at which the ball or pellet is crushed.

TABLE 5

Example No.	Adding Quantity of Binding Agent (wt %)	Rate of Reduction (%)	Swelling Index	Compressive strength (kg/pellet)
1	0.5	74.2	6.95	113
Reference Ex. (bentonite)	0.5	69.1	14.87	71

WHAT WE CLAIM IS:—

1. A method of producing ore pellets which comprises: adding to fine ore 0.05 to 4.0 wt % with respect to the total weight of fine ores of a binding agent, comprising water-soluble sulphonics acids obtained by sulfonation of condensed polycyclic hydrocarbons having an H/C atomic ratio of 0.4 to 1.25 and a mean molecular weight of 160 to 5,000 and/or salts of such sulphonics acids; pelletizing the resulting mixture; drying the thus produced ore pellets, and subjecting said dried ore pellets to firing.
2. A method of producing ore pellets as claimed in claim 1, in which from 2 to 10 wt % with respect to the weight of the ore, of lime (calculated as CaO) is also added to the fine ore.
3. A method of producing ore pellets as claimed in claim 1, in which from 2 to 10 wt %, based on the weight of the ore, of calcium hydroxide is also added to the powder ore.
4. A method of producing ore pellets as

claimed in claim 1, in which the finally obtained fired ore pellets are further subjected to reduction thereby to convert the fired ore pellets to reduced pellets.

5. A method as claimed in claim 1, in which there is further added to said binding agent an additional binder selected from bentonite, clay, sulfonated lignin or cement binder, or a surface active agent.

6. A method of producing ore pellets as claimed in claim 1, in which carbon powder of a quantity less than 20 wt % of the weight of the ore is added to the fine ore.

7. Ore pellets consisting essentially of pulverized crude ore and 0.05 to 4.0 wt % of a binding agent, the binder comprising water-soluble sulfonic acids prepared by sulfonating condensed polycyclic hydrocarbons having an H/C atomic ratio of 0.4 to 1.25 and a mean molecular weight of 160 to 5,000 and/or salts of such sulfonic acids.

8. Ore pellets as claimed in claim 6, in which the fine ore also contains 2 to 10 wt % with respect to the weight of the ore of lime.

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9. Ore pellets as claimed in claim 6, in which the fine ore also contains 2 to 10 wt % with respect to the weight of the ore of calcium hydroxide.
- 5 10. Reduced pellets prepared by reduction of the ore pellets according to claim 6.
11. Ore pellets as claimed in claim 6, in which the fine ore also contains carbon powder in a quantity which is less than 20 wt %
- 10 with respect to the weight of the ore.
12. Ore pellets substantially as herein described with reference to the Examples.
13. A method of producing ore pellets substantially as herein described with reference to the Examples.
14. Ore pellets when produced by a method as claimed in any of claims 1 to 6 or claim 13.

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